Experiment 6
Synthesis and Analysis of a Complex Iron Compound

Part Deux: Oxalate Content Analysis by Redox Titration

CH 204 Spring 2006

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But first...

Last week:

- Synthesis
- Metal complex coordination compounds
- Oxidation/Reduction (Redox) reactions
- Calculating theoretical yield and percent yield

Review of Redox Chemistry

Oxidation: Loss of electrons. Oxidation number increases (gets more positive).

Reduction - Gain of electrons. Oxidation number decreases (moves more negative).

Redox — A chemical reaction in which some atoms are oxidized and others are reduced. Individual atoms within compounds are oxidized or reduced.

What is an oxidation number?

A method for keeping track of the movement of electrons in redox reactions. It's like treating all compounds as if they're ionic compounds, even when we know they're not.

Each individual atom is assigned an oxidation number according to a few simple rules:

- Atoms in their elemental state have an oxidation number of zero.
- Monatomic ions have an oxidation state equal to the charge on the ion.
- All the oxidations states in a neutral molecule add up to zero.
- All the oxidation states in an ion add up to the charge on the ion.

Common Oxidation States

- Hydrogen is almost always +1.
  0 in elemental hydrogen (H_2 gas)
  -1 in metal hydrides such as $LiAlH_4$

- Oxygen is almost always −2.
  0 in elemental oxygen (O_2 gas)
  -1 in peroxides such as H-O-O-H

Some examples

$NaOH$ – O = -2, H = +1, Na = +1   Total = 0

CH_4 – H = +1 EACH, Total = 0, so C = -4

$KMnO_4$ – O = -2 EACH, K = +1, Total = 0, so Mn = +7

ClO_4^- – O = -2 EACH, Total = -1, so Cl = +7

ClO_3^- – O = -2 EACH, Total = -1, so Cl = +5

ClO_2^- – Cl = +3

ClO^- – Cl = +1

Cl^- – Cl = -1

Oxidizing Agents

An oxidizing agent is something that oxidizes other chemicals -- and therefore gets reduced itself. Strong oxidizing agents often have lots of oxygen atoms in them. Common examples include

$KMnO_4$, H_2O_2, $K_2Cr_2O_7$

$$MnO_4^- + 5\ e^- \longrightarrow Mn^{2+}$$

$$2H_2O_2 + 2e^- \longrightarrow 2H_2O$$

$$Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+}$$

These are **NASTY!** Nasty nasty nasty!

Reducing Agents

A reducing agent reduces other compounds and therefore gets oxidized itself. Hydrides are commonly used reducing agents, particularly Lithium Aluminum Hydride ($LiAlH_4$) and Sodium Borohydride ($NaBH_4$).

But wait, there's more!

Those were some common strong oxidizing and reducing agents, but under the right circumstances,

- Anything that can be reduced can act as an oxidizing agent
- Anything that can be oxidized can act as a reducing agent

Our redox reaction

We will use MnO_4^- to oxidize the oxalate ligands surrounding the Fe^{3+} from $C_2O_4^{2-}$ to CO_2.

Last week we oxidized Fe^{2+} to Fe^{3+} using hydrogen peroxide (H_2O_2) as the oxidizing agent.

Peroxide is not a strong enough oxidizer to oxidize the oxalate to CO_2, but permanganate is.

Oxidation half-reaction

Oxidation of $C_2O_4^{2-}$ to CO_2 is simple enough:

(Remember, half-reactions do not include the other reactant)

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

Reduction half-reaction

The oxidizing agent, MnO_4^-, gets reduced to Mn^{2+}

$MnO_4^- + 5e^- \rightarrow Mn^{2+}$ + a whole bunch of oxygens

In acidic solution,

$$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Add the two half reactions

First multiply the equations in order to balance out the electrons:

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \qquad \times 5$$

$$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad \times 2$$

$$5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$$

$$16H^+ + 2MnO_4^- + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$

The equation for the overall reaction is:

$$16H^+ + 2MnO_4^- + 5C_2O_4^{2-} \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Balancing redox reactions

- Identify which species is being oxidized and which one is being reduced.
- Separate them into half reactions (usually one of the half reactions is trivial to balance).
- Balance the main atom.
- Add H_2O to balance O, then add H^+ to balance H.
- Balance the charge using electrons.
- Add the two half-reactions (cancel out electrons)
- If the reaction takes place in basic solution add OH^- to both sides to turn H^+ into H_2O, and then and cross out redundant waters.

Balance this redox reaction

$$HBrO + Cd \rightarrow Br_2 + Cd^{2+}$$

Oxidation: $Cd \rightarrow Cd^{2+} + 2e^-$

Reduction: $HBrO$ + some electrons $\rightarrow Br_2$

Always balance in acidic solution

As easy as 1-2-4.

1) Balance the oxidized/reduced atoms
2) Balance oxygens using H_2O
3) Balance hydrogens using H^+
4) Balance charge using e^-

1) $2HBrO \rightarrow Br_2$
2) $2HBrO \rightarrow Br_2 + 2H_2O$
3) $2HBrO + 2H^+ \rightarrow Br_2 + 2H_2O$
4) $2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$

Add the two half-reactions

Oxidation: $Cd \rightarrow Cd^{2+} + 2e^-$

Reduction: $2HBrO + 2e^- + 2H^+ \rightarrow Br_2 + 2H_2O$

Overall Equation:

$$2HBrO + Cd + 2H^+ \rightarrow Cd^{2+} + Br_2 + 2H_2O$$

What if the solution is basic?

Here's what Whitten, Davis, Peck, and Stanley say:

To balance in a basic solution, for each O needed

(1) Add *two* OH^- to the side needing O

and

(2) Add *one* H_2O to the other side.

Then for each H needed,

(1) Add *one* H_2O to the side needing H

and

(2) Add *one* OH^- to the other side.

NO!

Here's what the new book suggests

"In basic solution, balance O by using H_2O; then balance H by adding H_2O to the side of each half reaction that needs H and adding OH^- to the other side.

"When we add . . . OH^- . . . $\rightarrow$ . . . H_2O . . . to a half-reaction, we are effectively adding one H atom to the right. "When we add . . . H_2O . . . $\rightarrow$ . . . OH^- . . . We are effectively adding one H atom to the left. Note that one H_2O molecule is added for each H atom needed."

TOO HARD!

Do it the E-Z way instead

Balance the equation in acidic solution,
and if it's supposed to be in basic solution,
just add enough OH^- to both sides
to get rid of all the H^+.

Just like this...

Permanagante is reduced to manganese (IV) oxide in basic solution:

$$MnO_4^{-2} \longrightarrow MnO_2$$

Balance O using H_2O: $MnO_4^- \longrightarrow MnO_2 + \mathbf{2H_2O}$

Balance H using H^+: $MnO_4^- + \mathbf{4H^+} \longrightarrow MnO_2 + 2H_2O$

Balance charge using e-: $MnO_4^- + 3e^- + 4H^+ \longrightarrow MnO_2 + 2H_2O$

Add one OH^- for every H+. Add OH^- to both sides!

$$MnO_4^- + 3e^- + 4H^+ + \mathbf{4OH^-} \rightarrow MnO_2 + 2H_2O + \mathbf{4OH^-}$$

Combine waters and delete redundant waters:

$$MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$$

Balancing redox reactions review

- Separate the reactants into half reactions (usually one of the half reactions is trivial to balance).
- Balance the main atom.
- Balance the half-reactions using H_2O to balance O, then use H^+ to balance H. Balance the charge with electrons.
- Add the two half-reactions – electrons must cancel.
- If necessary, convert acidic solution to basic by adding OH^- to both sides and crossing out spectator water molecules.

Today: Sample prep and three titrations

Land mine! 1:1 mixture of ethanol/water means mix them together in a beaker BEFORE you pour them in!

The $KMnO_4$ solution is already standardized and ready to go. Make sure you record the concentration!

Actual $KMnO_4$ concentration is about 0.035 M, not 0.02 M. Take 60 ml instead of 80 ml.